

# **PHYSICOCHEMICAL TREATMENT OF HIGH STRENGTH ORGANIC WASTEWATER**

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**MASTER OF TECHNOLOGY**

by

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to the

**DEPARTMENT OF CIVIL ENGINEERING**

**INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

**JUNE, 1988**

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CERTIFICATE

Certified that the work presented in this thesis entitled 'Physicochemical Treatment of High Strength Organic Wastewater' by Ravishankar B.R. has been carried out under my supervision and it has not been submitted elsewhere for a degree.

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## ABSTRACT

High strength organic wastewaters are difficult to be biologically treated due to high concentrations of degradable organic matter. Generally such wastes are diluted before biological treatment. An example of high strength organic wastes is dairy waste. In the present work, coagulation and adsorption processes were tried as a pretreatment with an objective of reducing the organic strength of dairy wastewater to a biologically treatable level.

Coagulants like Aluminum sulphate, Zinc sulphate, Ferric sulphate and Ferric chloride were used in an effort to bring down suspended and soluble COD. Alum gave a better suspended COD removal but zinc sulphate showed a better soluble COD removal. Ferric sulphate and Ferric chloride were not successful in removing either suspended or soluble COD. Sorbents like Sulphonated coal and Animal charcoal did not facilitate removal of soluble organics to any appreciable extent.

**Key Words:** High Strength Organic Waste, Dairy Waste, Pretreatment, Coagulation and Flocculation, Adsorption, Suspended Solids, COD, Soluble COD.

## 1. INTRODUCTION

The principal contaminants in regeneration of water from wastewater are suspended and colloidal solids, organic materials in soluble or insoluble form and susceptible for biodegradation, toxic materials and pathogenic organisms. Biological methods for removal of biodegradables is a commonly accepted practice. However, biological systems operate successfully in a narrow range of environmental conditions and are limited in application, unless the waste parameters are brought to within the tolerable ranges of microorganisms. A number of liquid wastes are known to be difficult to treat biologically due to high concentrations of degradable organic matter. Such wastes are generally termed as high Biochemical Oxygen Demand (BOD) wastes and include liquid wastes from sugar factories, breweries, distilleries, dairies, tanneries and the like, which have BOD values in thousands. Dilution followed by biological treatment is adopted in these cases, increasing the volumes of wastes enormously.

Understandably, physicochemical pretreatment to bring down the BOD of such high strength wastewaters within the limits of biological treatment would be a desirable alternative.

An example of high BOD wastes is the dairy waste. Milk contains carbohydrates such as lactose, proteins such as casein and fats in addition to various minerals and majority of vitamins (Ling, 1956). These can be readily degraded by the microorganisms found in nature. The BOD of wholesome milk is of the

order of 100,000 mg/l. Due to its high BOD:COD (Chemical Oxygen Demand) ratio, the dairy waste can be treated efficiently by biological processes (Mohanrao and Subramanyam, 1972). Hence this waste was considered for the present investigation.

To what extent can the BOD be brought down and whether any soluble organics can be removed by physico-chemical methods were the problems taken up for investigation.

Chemical precipitation is an established method of removal of suspended and colloidal materials. While this process of destabilization and agglomeration of suspended particles is going on, it is anticipated that some dissolved organic matter may also be removed by various mechanisms like adsorption, metal binding, denaturation and the like. It is known that different coagulants have different affinities for hydrophilic and hydrophobic colloids. Keeping some of these points in view, the experiments were planned to yield data on removal of suspended and soluble organic matter using different coagulants.

The objective of the present work was reducing the BOD and the aim was not to produce an effluent for final discharge but to work out a pretreatment method to reduce BOD to the desired range.

## 2. LITERATURE REVIEW

One of the industrial wastes with known high BOD value is the dairy waste. Because of the location of a dairy in Kanpur, it was felt that this industrial waste can be used for experimentation. Hence, given below are the salient characteristics and work carried out on dairy wastes.

### 2.1 Wastewater Characteristics:

Dairy wastes comprise of washwater from milk cans, equipment, bottles and floors; components of spilled milk, spoiled milk, skimmed milk, whey, buttermilk and wastes of any special process. The volume and the composition of the wastewater depends upon the capacity of industry, different types of products made, the care with which the processes are conducted (to avoid leakages and spillages) and the amount of water used for washing cans, bottles, milk storage tanks, pasteurising units, pipelines, floors etc. and hence varies considerably with time and industry to industry. Milk itself being a mixture of various components like lactose, fat, casein and inorganic salts shows considerable variation in its general characteristics. Moreover, changes in physical condition of some constituents may modify their normal behaviour (Ling, 1956). Hence there are different reports on characteristics of dairy wastewaters.

Dairy waste contains mostly biodegradable organics. Hence the accent is on BOD and COD values. Mohanrao and Subramanyam (1972) have reported characteristics of small, medium and large dairies (Tables 2.1, 2.2 and 2.3), the BOD and COD of which

Table 2.1: Characteristics of the Combined Wastes from a Small Size Dairy\* (Mohanrao and Subrahmanyam, 1972)

Volume of Milk Processed = 12,800 l/d.

Waste Volume = 3.6 l/l of milk.

(All values except pH are expressed in mg/l)

	Combined V
pH	8.1
Total solids	2,730
Volatile solids	2,205
Suspended solids	1,810
Volatile suspended solids	1,660
Alkalinity as $\text{CaCO}_3$	220
Volatile acids as $(\text{CH}_3\text{COOH})$	20
COD	4,510
BOD	3,070
COD:BOD	1.47
BOD rate constant (K/day)	0.19
Total nitrogen as (N)	1,080
Total phosphorus as (P)	110
Sulphates ( $\text{SO}_4^{2-}$ )	45
Fat	1,390

\* Average values of 10 composite samples. This dairy is primarily a pasteurisation and bottling plant and has severe restriction on its water supply.

Table 2.2: Characteristics of Individual Wastes (6) from a Medium-Size Dairy \* (60,000 l of Milk/d) (Mohanrao and Subrahmanyam, 1972)

(All values except pH are in mg/l)

	Butter Washings	Rejected Milk	Milk Bottling Waste
pH	4.7	6.6	7.8
Alkalinity to pH 8.3	Nil	Nil	Nil
	4.5	100	10,350
Total solids	13,820	85,920	2560
Total volatile solids	10,640	75,500	2000
Fixed solids	3,180	10,420	560
Suspended solids	5,112	34,904	1380
Volatile suspended solids	4,832	33,280	1220
BOD at 37°C	10,000	62,000	620
COD	16,000	88,000	1000
Ca <sup>++</sup>	180	900	140
Mg <sup>++</sup>	12	474	49
COD:BOD	1.60	1.33	1.61

\* Mostly bottling, preparation of butter and casein from soured milk.

Table 2.3: Characteristics of the Individual Wastes from a Large Dairy\* (Mohanrao and Subrahmanyam, 1972)

(All values except pH are expressed in mg/l)

	Receiving and Pasteurisation Units	Cheese Plant	Butter and Ghee Units	Casein Plant	Combined Effluent
pH	8.2	6.7	7.1	7.7	8.0
Colour	White	White	Brown	Clear	White
Total solids	3640	2300	3460	680	1690
Volatile solids %	77	29	72	62	67
Suspended solids	1320	600	2240	160	690
Alkalinity as $\text{CaCO}_3$	500	490	450	490	590
Oxygen absorbed	437	483	90	9	120
BOD	1820	2150	1377	200	816
COD	2657	3188	3218	372	1340
Total nitrogen	-	-	-	-	84
Phosphates	10	12	2	5	12
Oil and grease	690	520	1320	Nil	290
Chlorides	105	105	105	70	112
COD:BOD	1.46	1.48	2.33	1.86	1.65

\* A product oriented dairy processing about 360,000 l/d of milk.  
 Flow: 6-8 litres of waste per litre of milk processed.  
 Temperature: 29.5 - 35.5°C. Average 32.8°C.

varies from 800 to 3000 mg/l and 1300 to 4500 mg/l respectively. Verma et.al. (1974) have reported a BOD of 1500 mg/l and a COD of 2400 mg/l in a dairy in U.P. Two dairies in Himachal Pradesh at Chakkar and Shimla have reported BOD varying from 230 mg/l to 2800 mg/l (Correspondence with the Himachal Pradesh State Cooperative Milk Producers' Federation Ltd., 1986). The strength of wastewater depends on the volume of water used in a dairy. Saxena and Subramaniam (1978) observe that about 10 litres of water is used per litre of milk and reported an average value of 1000-2000 mg/l BOD.

## 2.2 Effect of Dairy Waste:

### 2.2.1 On Inland Surface Waters:

The dissolved oxygen of streams and rivers is likely to be depleted if the water body contains organic matter which uses the dissolved oxygen for biodegradation. Though natural processes in the stream such as the turbulence of the river, molecular diffusion from air and production of oxygen due to photosynthesis activity by the plankton replenish the oxygen in the system, if the rate of deoxygenation is greater than reoxygenation, fish kills can occur and anaerobicity can set in. Dairy wastes contain soaps and detergents, lactic acid and butyric acids, sugar, whey and other substances that will cause water pollution directly or indirectly. Putrefaction due to rapid degradation of lactose and the production of lactic acid and butyric acids lead to foul odours (Mohanrao, 1972). It was reported that at a dilution of 1:15, dairy wastes (excluding

whey) had distressing effects on fish (Doudoroff and Katz, 1950). Lactic acid can be toxic to fish at around 600 mg/l and low dissolved oxygen. Butyric acid - a product of anaerobic metabolism - has very unpleasant rancid odour. Beyond 100 mg/l concentration, it is known to adversely affect and above 400 mg/l kill trout fish. It is also known to affect Scenedesmus algae (Mohanrao, 1972).

#### 2.2.2 In Public Sewers:

The temperature of the dairy waste from 30° to 40°C is ideal for the growth of bacteria. As the waste contains significant amount of carbohydrates and the temperature is ideal, the possibility of sewage mixture becoming septic in the sewer itself is very great and this may need additional pre-aeration in the sewage treatment plant. Because of much higher strength, the additional BOD load on treatment plant has to be considered (Mohanrao, 1972).

### 2.3 Treatment:

#### 2.3.1 General:

As is evident from high BOD:COD ratio, dairy wastes are readily amenable to biological treatment. A lot of work has been reported on treatment of dairy waste by biological methods. Nemerow (1978) has given a comprehensive review of conventional treatment methods like aeration, trickling filter treatment, activated sludge treatment, land disposal, lagooning and anaerobic digestion.

Bull et.al. (1981) in their review of treatment methods of dairy wastewater have referred to less common methods of waste treatment like Rotating Biological Contactors (RBC), ion exchange, apart from chemical coagulation. They report that anaerobic treatment is not a wide-spread practice as the anaerobic process is susceptible to failure due to volatile acid accumulation. Wherever used, these have been a first stage treatment followed by aerobic system.

However, a few papers have reported the use of anaerobic packed bed filters for dairy waste treatment. Taori et.al. (1983) have achieved 88 percent COD removal in a pilot plant study of anaerobic packed bed upflow filters. Cardoba et.al. (1984) have reported 85 percent COD removal with horizontal anaerobic filters.

Alagarsamy and Bhalerao (1972) have reported as much as 95 to 98 percent BOD removal from dairy wastewater by oxidation ditch - an extended aeration process.

Agarwal and Suriapandian (1981) studied the treatment of dairy wastewater in a laboratory scale RBC. They obtained a 90 percent removal of COD.

Satish Chand and Mehrotra (1988) have reported about 85 percent BOD removal from synthetic dairy waste by aerobic fluidised bed in a pilot plant study.

### 2.3.2 Chemical Treatment:

A few of the common coagulants like Aluminum sulphate, Ferric chloride, Ferric sulphate, Zinc sulphate and Lime have been considered. Madhu Rani Sharma (1983) and Ahmad (1985) have made an extensive literature survey on these coagulants.

Not much has been reported about chemical treatment methods of dairy wastes. Mihaltz and Czebo (1984) report that poultry and meat industry effluents with COD of 1500-2500 mg/l were treated in a dissolved air flotator with addition of 300 mg/l ferric chloride or aluminum sulphate to get a COD removal of 85-87 percent.

Singh et.al. (1983) studied a two step treatment of an effluent from vanaspati ghee manufacturing unit, with chemical coagulation/de-emulsification followed by biological oxidation to get 90 percent effective recovery of oil, which could be used as a fuel. Alum, ferrous sulphate and ferric chloride were used for chemical treatment. Ronkainen (1976) used about 200-220 mg/l ferric chloride in a dairy wastewater pond to get around 90 percent reduction in BOD and phosphorus contents.

Tabakov (1979, 1984, 1984a) reports treatment of dairy wastewater with the use of electrocoagulation and electroflocculation. About 83 percent COD removal was observed.

### 3. MATERIALS, METHODS AND EXPERIMENTS

#### 3.1 Materials:

##### 3.1.1 Dairy Wastewater:

Effluent from 'Parag' dairy (Kanpur Sahakari Milk Board Ltd., Kanpur) was used for the study. The effluent was a combination of wastewaters from pasteurization plant, washing section and Miltone (a proteinaceous drink prepared with toned milk and ground-nut protein extract) section.

##### 3.1.2 Synthetic Wastewater:

'Parag' milk available in the market was diluted with tap water to obtain the synthetic dairy wastewater.

##### 3.1.3 Chemical Coagulants:

Aluminum sulphate (commonly known as Alum), Zinc sulphate, Ferric sulphate, Ferric chloride and Commercial lime were used as coagulants. Commercial lime was also used as a coagulant aid. General details of the coagulants are given in Table 3.1.

All other chemicals used were of analytical grade.

##### 3.1.4 Sorbents:

Sulphonated coal and commercially available Animal charcoal were used for adsorption tests. The Sulphonated coal used had been prepared in the laboratory (Suneeth Kumar, 1987) and was of size 250-300  $\mu\text{m}$ .

##### 3.1.5 Equipment:

The equipments used in this study are listed below.

- (i) Jar test apparatus                            Phipps and Bird Inc., U.S.A.

Table 3.1: General Details of Chemical Coagulants Used

Chemical	Formula	Percent purity	Name of the manufacturer
Aluminum sulphate	$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	97	Thomas Baker (Chemicals) Pvt. Ltd., Bombay, India
Ferric chloride	$\text{FeCl}_3$	96	Sarabhai M. Chemicals, Baroda, India
Zinc sulphate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	99	Sarabhai M. Chemicals, Baroda, India
Ferric sulphate	$\text{Fe}_2(\text{SO}_4)_3$	-	Reidel-Deëfachag Seelze-Hannover, W. Germany

(ii)	Turbidimeter	Model 2100, Hach Chemical Co., Iowa, U.S.A.
(iii)	pH meter	Elico Digital pH meter, Model LI-120, Elico Pvt. Ltd., Hyderabad
(iv)	Millipore filter assembly and filter paper	Millipore Corporation Bedford, Massachusetts, U.S.A.

### 3.2 Method of Analyses:

In most of the cases, samples were analysed immediately after the experiments. In a few cases when samples were analysed after some lapse of time, preservation procedure prescribed by Standard Methods (1984) was followed.

#### 3.2.1 Turbidity Measurements:

Measurement of turbidity were taken immediately after sample collection from experiments. The instrument, Hach turbidimeter, was standardised every time before use with the help of standard turbidity suspensions prepared as per the Standard Methods (1984).

#### 3.2.2 pH Measurement:

pH was measured using a pH meter. The instrument, Systronics pH meter, was standardised every time before use with commercial buffer solutions.

#### 3.2.3 Chemical Oxygen Demand (COD):

COD analysis was conducted as per the method given in Standard Methods (1984). A sample volume of 20 ml or a

fraction diluted to 20 ml was used for the analysis. Soluble COD was determined after filtering the samples through 0.45  $\mu$  membrane filter paper.

#### 3.2.4 Biochemical Oxygen Demand (BOD):

The 5 day BOD analysis was conducted as per the method given in Standard Methods (1984).

#### 3.2.5 Alkalinity:

Alkalinity was determined by indicator method specified in Standard Methods (1984). The indicators used were phenolphthalein and methyl orange.

#### 3.2.6 Total and Suspended Solids:

Total solids and suspended solids were determined as per the Standard Methods (1984).

### 3.3 Experimental Procedure:

#### 3.3.1 Standard Jar Test Procedure:

The six place jar test apparatus was used for coagulation experiments. Dairy waste brought was allowed to settle for one hour and the supernatant was used for jar tests. Each jar contained 500 ml of sample. Apposite quantities of coagulants were administered into the jars keeping one jar as a control. A rapid mixing at 100 rpm for one minute was followed by slow mixing at 30 rpm for twenty minutes. The residual turbidity after thirty minutes of settling was used as the index of the extent of coagulation. About 50 ml of sample was collected from each jar with the help of a pipette for analyses.

The required amount of the coagulants were added during rapid mixing. All the coagulants were added in solution form. Lime suspension was thoroughly mixed before addition.

### 3.3.2 Adsorption Studies:

To find out the adsorption of soluble COD on sorbents, various doses of sorbents ranging from 300-4000 mg/l were placed in sampling bottles containing 50 ml of alum clarified supernatants. Rotary shaker ( $16\frac{1}{2}$  rpm) was used to ensure thorough mixing. After 2 hours, the samples were filtered through membrane filter to remove the sorbents added before analysing for COD.

#### 4. RESULTS AND DISCUSSION

Physico-chemical methods are used as primary treatment units to be followed by biological methods for treating most of the biodegradable organic wastes. Since the range of tolerance for input concentrations and various parameters in biological treatment processes is narrowly restricted, certain amount of reduction in BOD and COD values, adjustment of pH, temperature, volume and/or concentration equalization is needed before biological treatment can be adopted. This is achieved by various methods like the use of holding tanks, chemicals, simple dilution etc. The last method naturally increases the volume of wastes enormously leading to economic non viability of biological treatment systems.

Chemical coagulation and flocculation is a widely used method in water treatment and was popular in the early stages of development of wastewater treatment systems. Ignored for a long time, due to various reasons like handling and cost of chemicals, close supervision requirements etc., the methods are again gaining attention in recent years to tackle special problems like heavy metal removal, polishing effluents to a better desired level of treatment for parameters like phosphates etc. Most widely used coagulant chemical is aluminum sulphate, followed by iron salts, lime and magnesium salts. Removal of suspended inorganic and organic materials represented by turbidity measurement by coagulation and flocculation is well known. Use of

coagulants to remove colour, representing soluble organics is also reported in literature (Metcalf and Eddy, 1979).

Wastewater suspended solids are divided into organic, inorganic, settleable, filterable or colloidal according to their behaviour. Colloids can be differentiated into two types. The hydrophobic colloids, which are common in surface waters, consist chiefly of inorganic materials. On the other hand the suspended and dissolved solids, being the degradation products of food materials like polysaccharides, fats and proteins, are mostly organic macromolecules. Some of these colloids are hydrophilic in nature. Owing to this innate natural differences between the two types of colloids, some behavioural differences are bound to occur even if they are not pronounced sometimes. It is known that particles with a size above  $10^{-2}$  mm form settleable solids, those between  $10^{-6}$  mm and  $10^{-3}$  mm are considered to be colloidal, while below  $10^{-7}$  mm, they are molecular and hence form dissolved solids. Typical classification of solids found in medium strength wastewater are listed in Figure 4.1. Because of electrokinetic properties, colloids remain in suspension. Many hydrophilic colloids function as protective colloids and "coagulation of such system requires rather drastic treatment with massive doses of coagulant salts, often ten to twenty times the amount used in conventional water treatment. Information concerning the action of coagulants on many hydrophilic colloids is lacking. Further research is needed" (Sawyer and McCarty, 1978). In an attempt to find out physicochemical methods for reducing

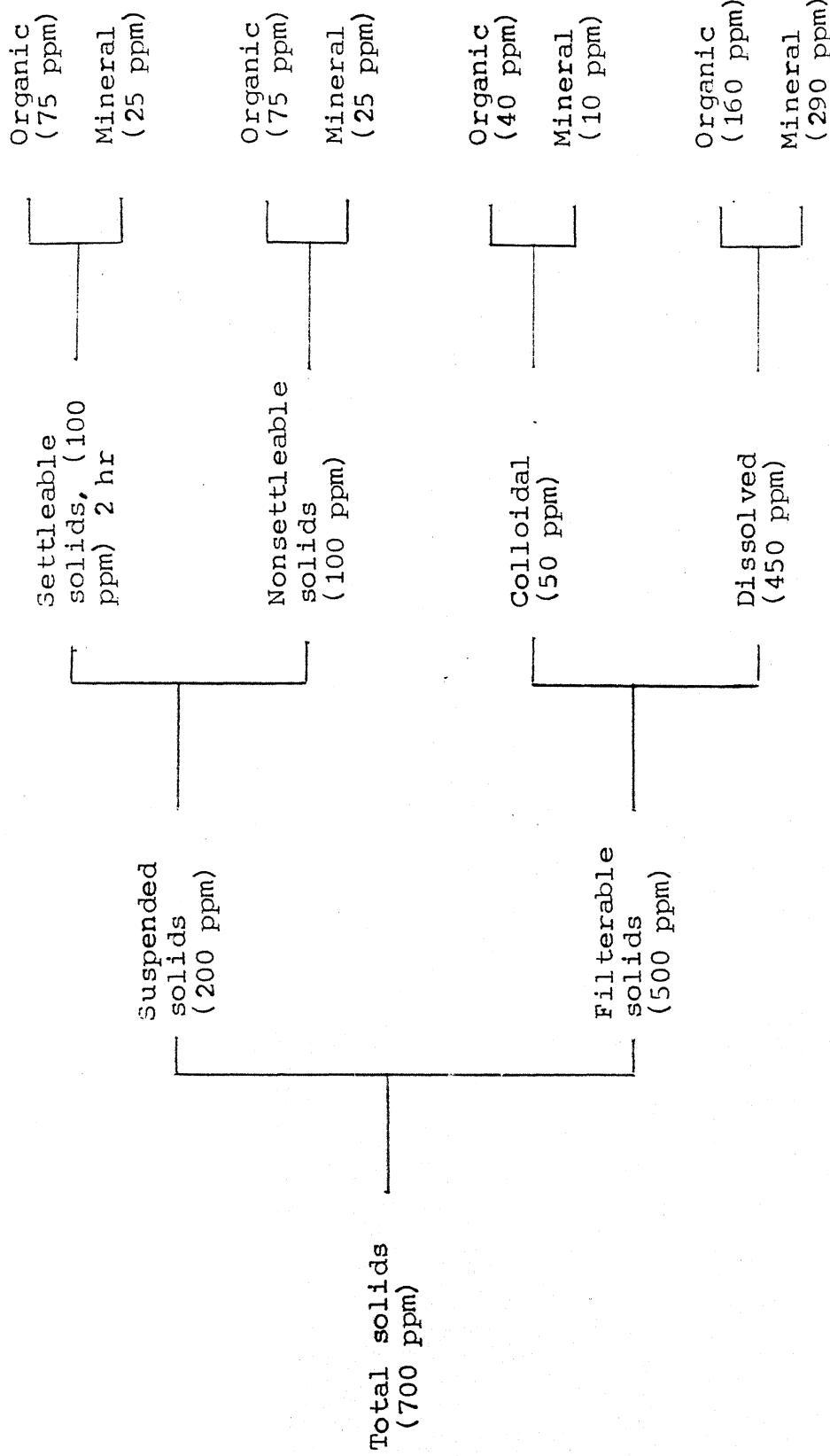


Figure 4.1: Classification of Solids Found in Medium Strength Sewage (Metcalf and Eddy, 1972).

suspended solids represented by turbidity and organic materials represented by COD measurements to an acceptable level for biological treatment, experiments were carried out with dairy wastes collected from a local dairy. After determining the approximate dose of a coagulant, attempts were made to find out if any soluble organics have also been removed along with suspended materials by estimating soluble COD values.

It was found and also reported in literature, a wide variation of COD and turbidity values of actual wastes collected at different times (Mohanrao, 1972). Most important was the soluble organics variation which were sometimes more and some<sup>times</sup> very less. For this reason, not realized earlier, there was variation between experimental results causing confusion in the validity and reproducibility of results. Many experiments were discarded and only experiments with natural wastes of similar characteristics were taken for presentation in the thesis. The inference from this observation is the need to have an equalization tank in the field conditions. Wherever it was possible, average values of three experiments were taken from wastewater of similar characteristics.

Characteristics of a typical waste used for the experiments are shown in Table 4.1.

#### 4.1 Simple Sedimentation:

It was observed from the characteristics of dairy wastes used for experiments that they had high suspended solids content and a portion of them were settleable. Hence, the wastes were

Table 4.1: Characteristics of Combined Wastewater of 'Parag' Dairy

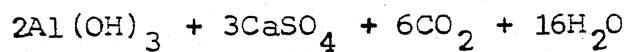
Colour	Milky white
Turbidity	200 NTU
pH	6.85
Total alkalinity as $\text{CaCO}_3$	516 mg/l
Total solids	820 mg/l
Settleable solids	2.5 ml/l
BOD	1104 mg/l
COD	1600 mg/l
BOD:COD	0.69

allowed to settle for one hour and COD of the supernatants were also found out. These supernatants were used in subsequent coagulation experiments. Table 4.2 gives the variation in the characteristics of dairy wastes brought on different days over a period of nine months. It is evident on the face of it that all the three parameters monitored vary considerably.

The presence of settleable solids may be attributed to the waste from a special process of manufacturing Miltone in which protein extract from groundnut is used. The wastewater from this process consists of groundnut waste and also some protein extract. This groundnut wastes is responsible for the settleable property observed. Probably due to different amounts of this waste in the samples collected, there is a large variation of percentage turbidity removal by simple sedimentation. But, as is observed, this turbidity removal has no direct correlation with COD removal. Probably this is because of the variation in soluble and suspended COD ratio in the sample and some non oxidisable material in the groundnut powder.

#### 4.2 Experiments with Alum:

Initial experiments in screening coagulants were started with most popular chemical, aluminum sulphate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ ), commonly referred in water treatment as alum. The chemical reaction of alum with the natural alkalinity of the medium is



Sl. No.	pH	Turbidity NTU	COD mg/1	Supernatant Turbidity NTU	Supernatant COD mg/1	Soluble COD mg/1	Percent Turbidity Removal	Percent COD Removal
1	6.12	135	2,878.5	50	1,425.9	-	62.9	50.5
2	6.90	55	328.0	20	186.1	-	63.6	43.2
3	6.70	95	6,692.8	90	3,769.8	-	5.2	43.6
4	5.85	150	3,824.0	100	1,932.5	-	33.3	49.5
5	5.90	180	-	130	3,843.0	-	27.7	-
6	6.20	170	2,701.0	120	1,338.8	-	29.4	50.4
7	5.33	100	3,940.0	80	1,611.0	-	20.0	59.1
8	7.70	120	1,527.0	80	700.0	-	33.3	54.2
9	6.10	240	10,700.0	150	3,100.0	2,200.0	37.5	71.2
10	6.00	110	8,327.0	80	6,556.6	1,714.3	27.3	21.3
11	6.85	850	20,871.0	600	16,972.0	11,880.4	29.4	18.7
12	6.39	60 (1:50)	6,465.5	60 (1:50)	5,418.0	1,724.3	-	16.2
13	6.07	900	20,812.0	800	16,751.0	-	11.1	19.5
14	4.97	750	11,674.0	200	6,561.1	-	73.3	43.8

The solubility equilibria of amorphous  $\text{Al(OH)}_3(s)$  is given in Figure 4.2. Preliminary screening for alum dose was carried out with concentrations varying from zero to 1000 mg/l.

The results are presented in Figure 4.3 in which the turbidity and COD removals seemed to be good at 200 mg/l of alum. The alkalinity of the waste was above 500 mg/l and was sufficient for alum coagulation. Even though turbidity is removed almost completely (96 percent), removal of COD was only 60 percent.

Variation of alum dose from zero to 200 mg/l gave varying results with samples obtained on different days (Figures 4.4, 4.5 and 4.6). It can be seen that there is a slight variation of pH and initial values of turbidity and COD. The significant point that emerged out of these experiments is that no direct correlation could be seen in turbidity removal and COD removals, indicating that the nature of suspended solids as well as soluble organics may have significance in these experimental results. It is obvious that removal of turbidity does not necessarily mean removal of organics when these are perhaps in the soluble form. To elucidate this point, the following experiment with alum dose variation from zero to 250 mg/l was conducted taking into account the soluble and suspended COD (Figure 4.7) which indicates that soluble COD is not removed to any appreciable extent. The experiments with alum indicate that the turbidity could be removed anywhere from 70-90 percent or more, total COD can only be removed from 20-55 percent and soluble COD is not significantly removed in the process.

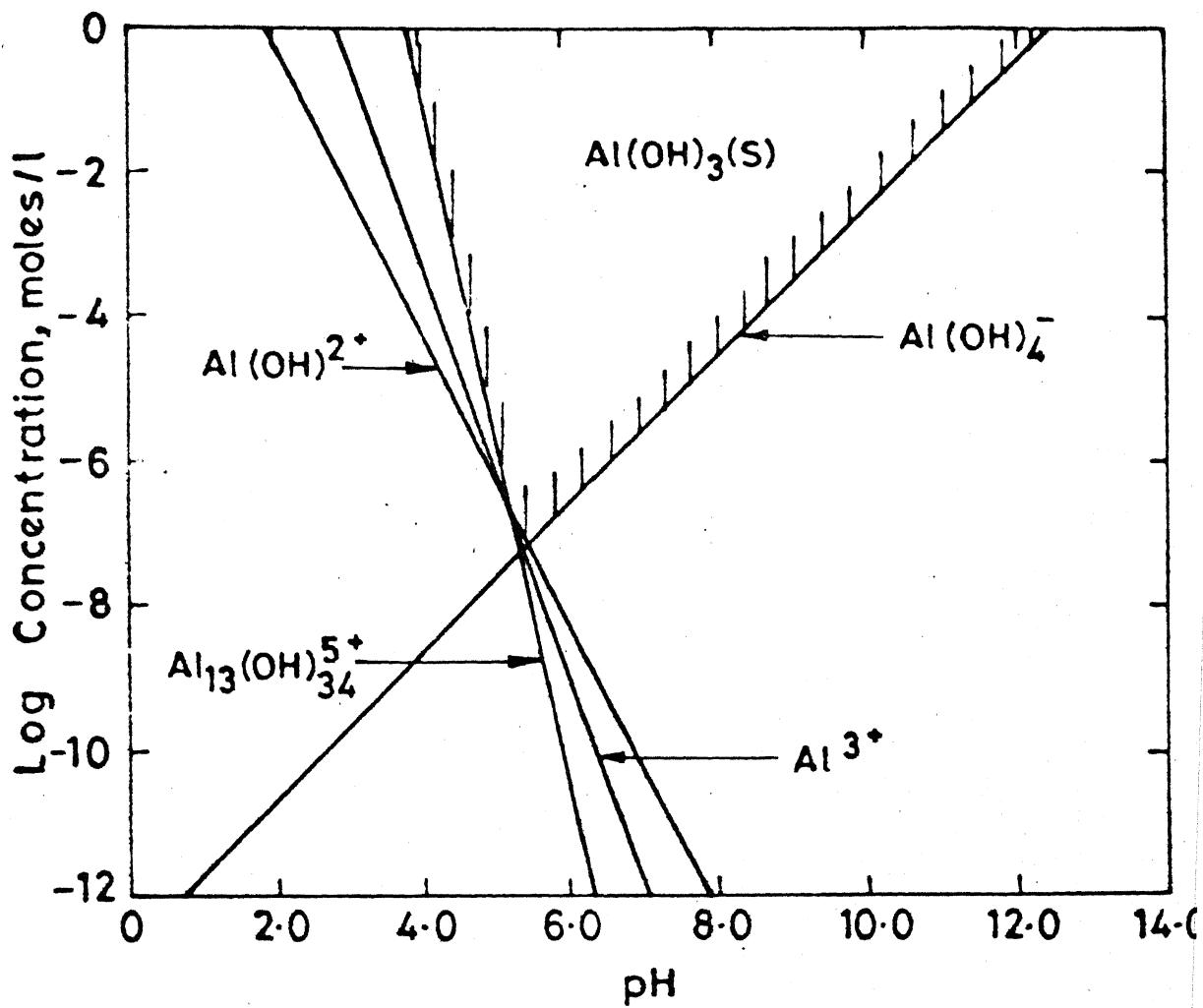


Fig. 4.2 Solubility Equilibria of Amorphous  $\text{Al(OH)}_3(\text{s})$  at 25 °C (Weber, 1972).

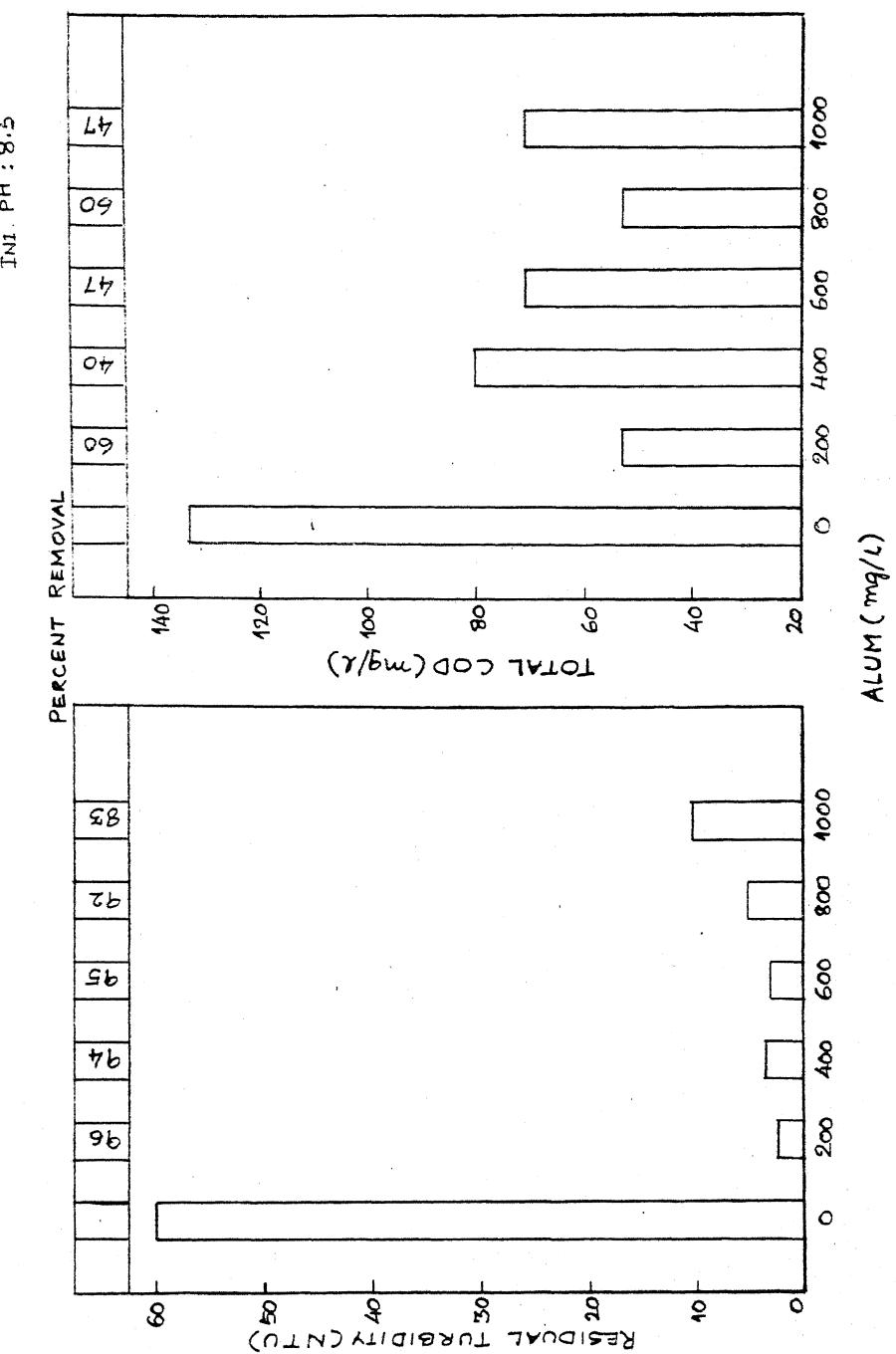


Fig. 4.3 : Removal of Turbidity and Total COD by Alum Coagulation -  
Preliminary test.

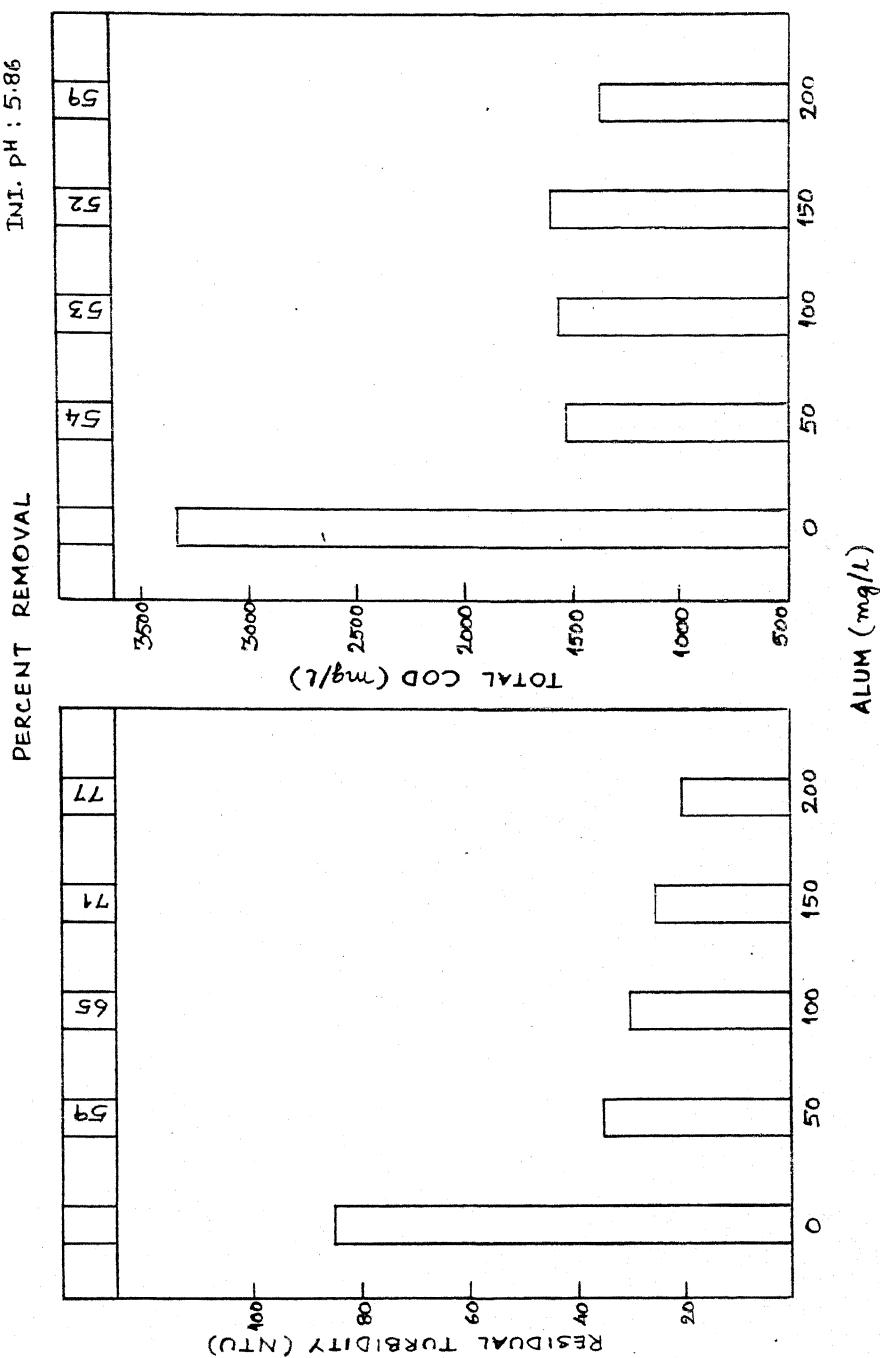


FIG. 4.4 : Removal of turbidity and Total COD by Alum Coagulation  
— Sample-1

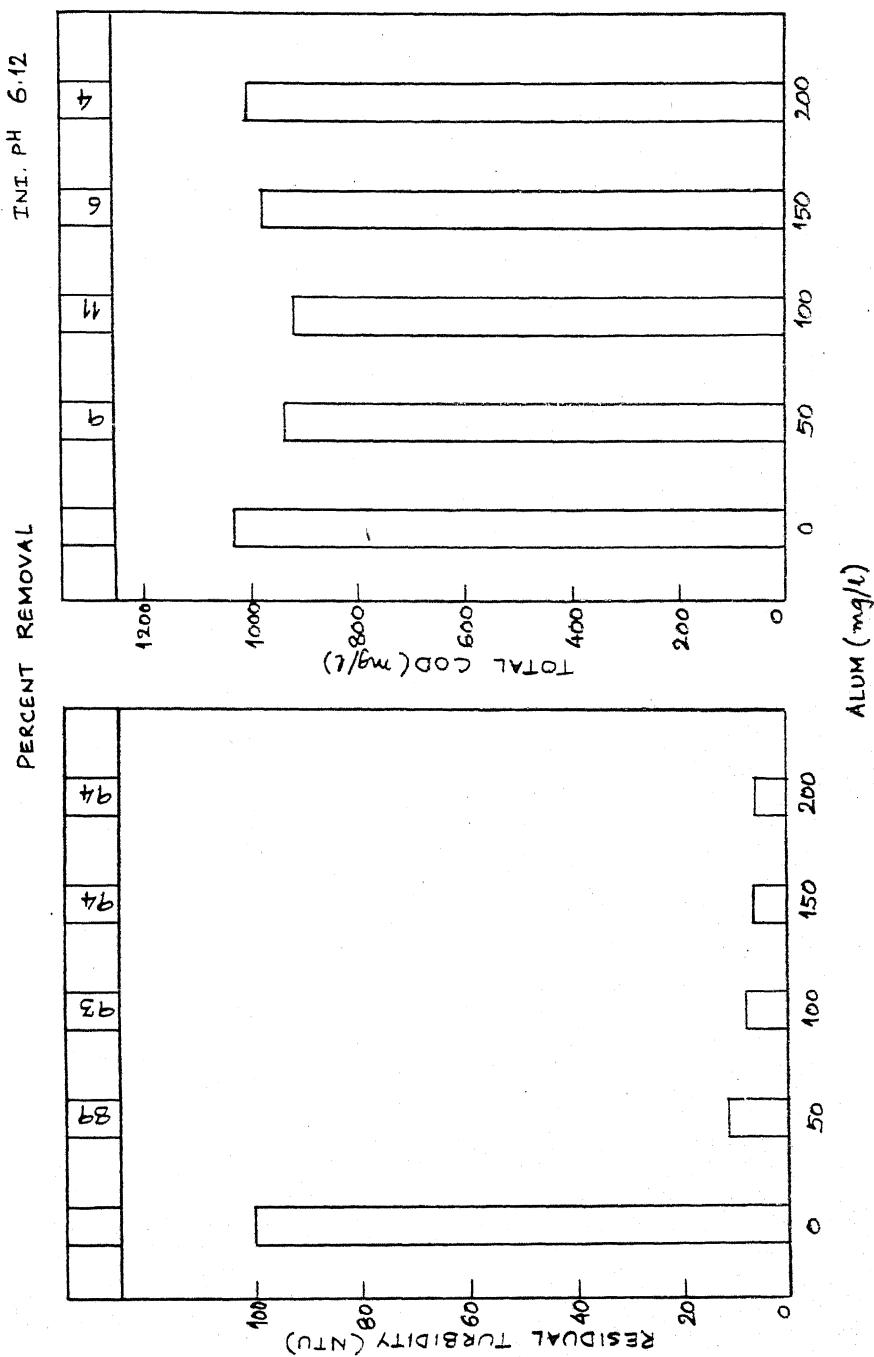


Fig. 4.5 : Removal of turbidity and Total COD by Alum Coagulation  
- Sample-2.

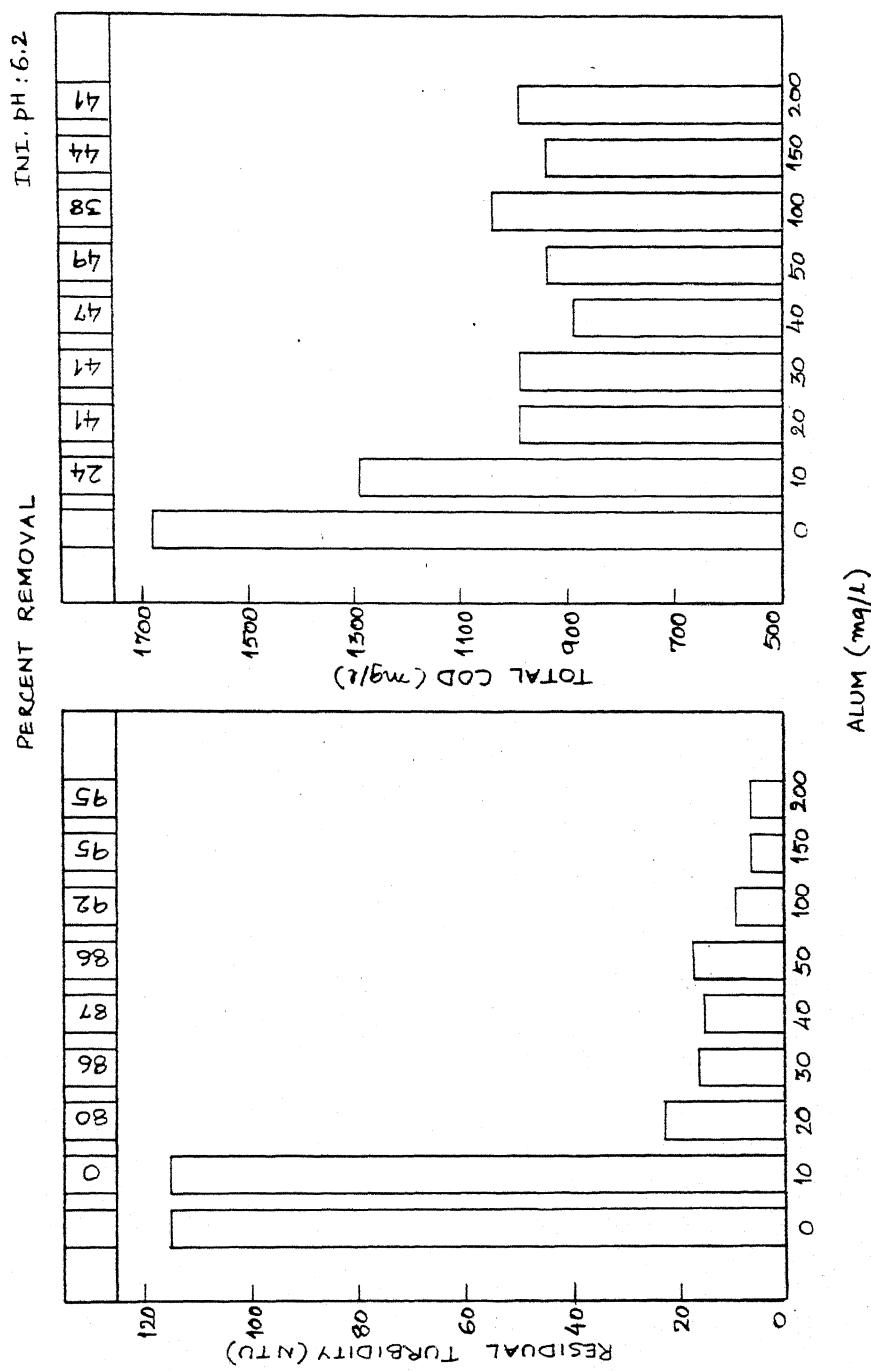


Fig. 4.6 : Removal of Turbidity and Total COD by Alum Coagulation  
— Sample-3.

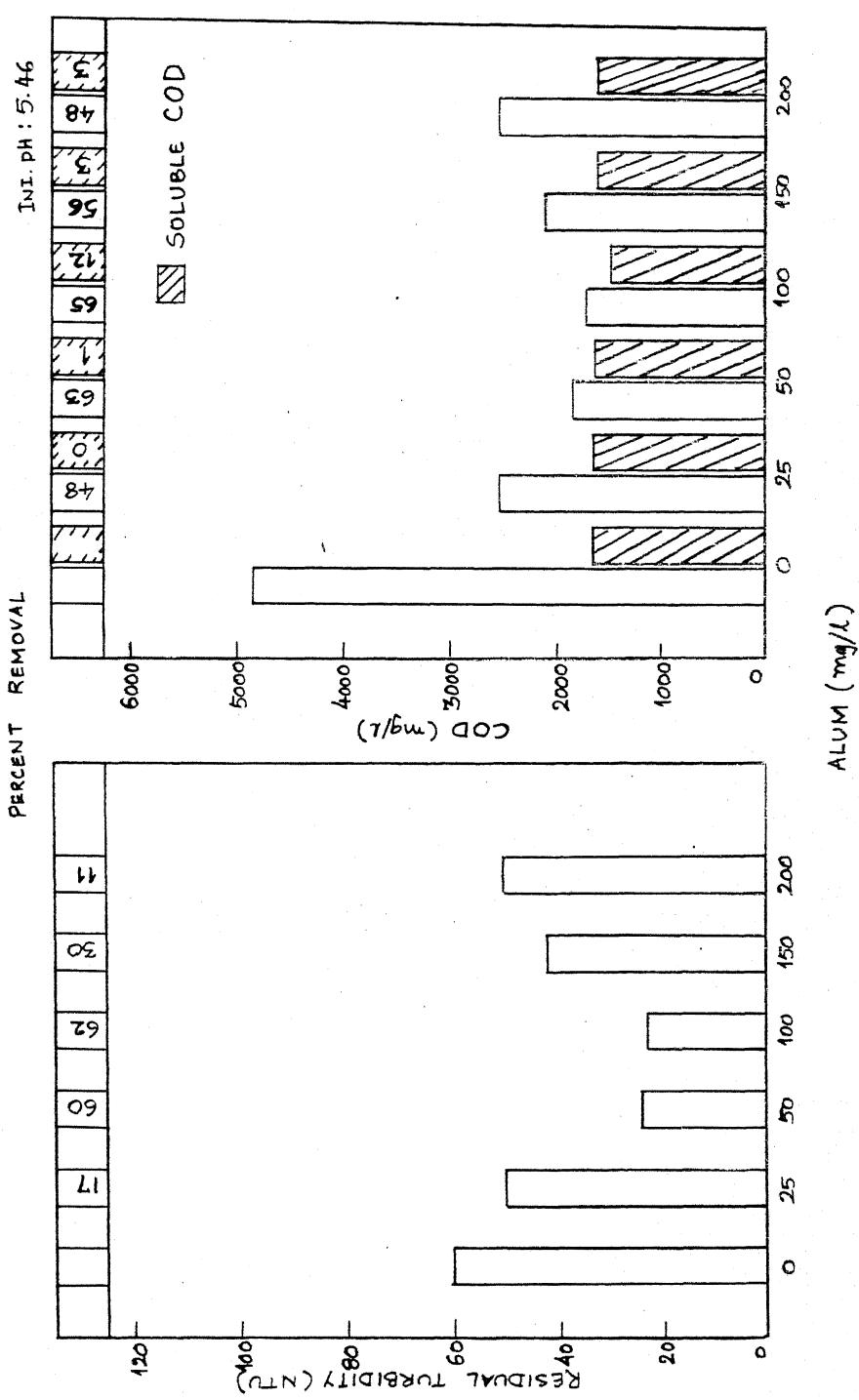
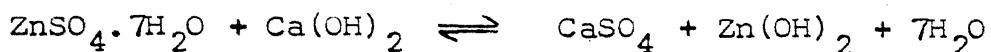


Fig. 4.7 : Removal of Soluble COD by Alum Coagulation.

#### 4.3 Experiments with Zinc Sulphate:

Zinc sulphate has been reported to give good removal of sewage colloids which are organic hydrophilic colloids (Ahmad, 1985). Milk solids are also of a similar nature. Moreover zinc is known to bind protamines and other proteins. Hence zinc salts were used for coagulation and flocculation with a hope that some dissolved solids may also be removed. The chemical reaction of zinc sulphate with the natural alkalinity of the medium is



Keeping in view the optimum pH at which the zinc hydroxide solubility is minimum, i.e., between pH 9 to 10 (Figure 4.8), commercial lime was used as a coagulant aid.

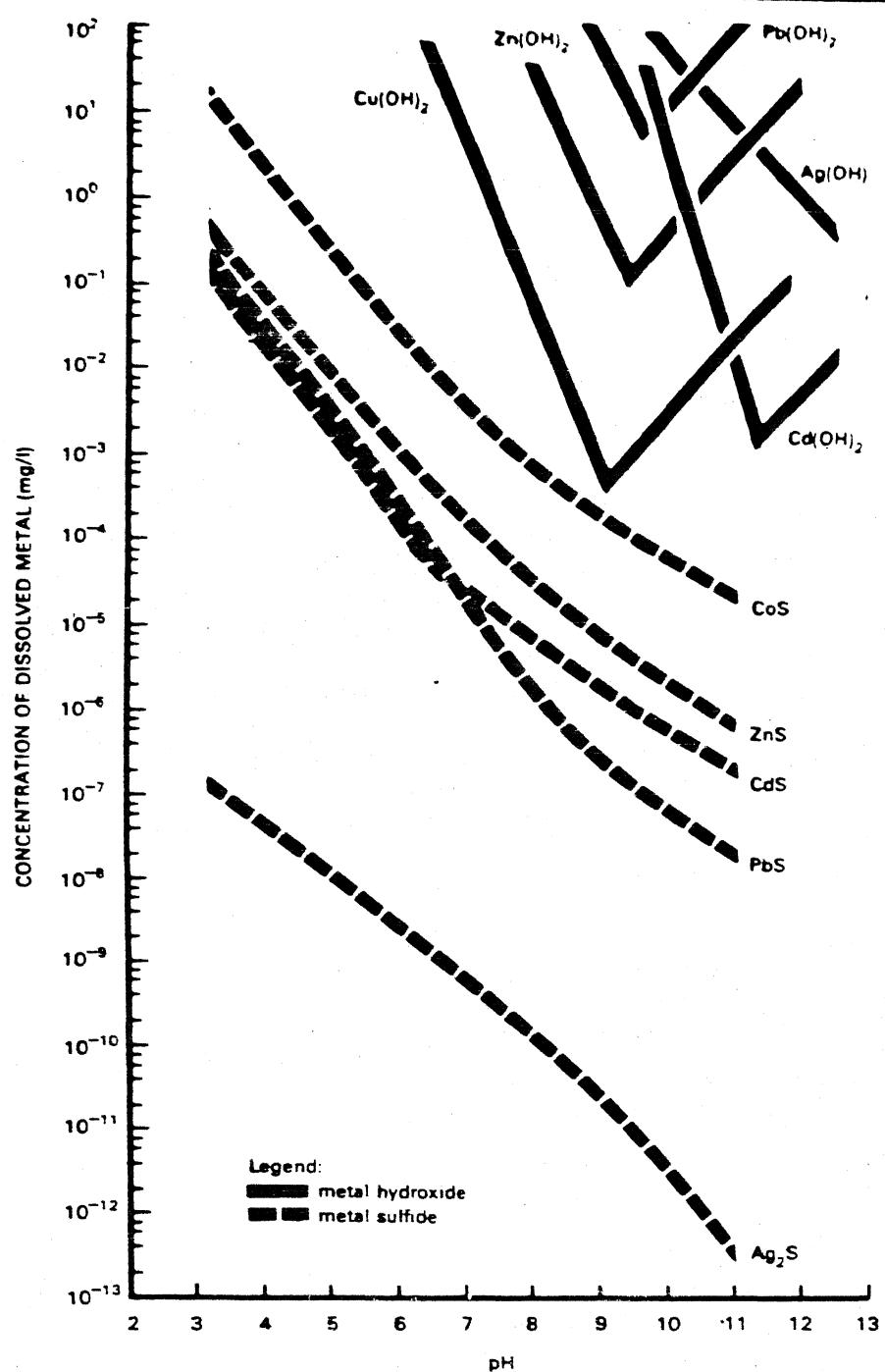
Slop tests were conducted with zinc sulphate dosage varying from zero to 100 mg/l and about 400 mg/l of lime (to increase alkalinity and pH). The results indicated that the dose 30 mg/l gave the best removal of turbidity. Also, a yellowish colour development was observed at higher doses of zinc sulphate. Hence doses upto 30 mg/l only were considered for further experiments.

Jar tests were conducted with varying zinc sulphate and lime concentrations. A dosage of 10-30 mg/l zinc sulphate alone and at lower concentrations of lime did not facilitate any removal of suspended particles.

Experiments were carried out with zinc sulphate concentration of 20 mg/l and 30 mg/l and lime concentrations varying from 100 to 600 mg/l. The result of a series of jar tests conducted with these dosages has been shown in Table 4.3. One important observation was that even at these dosages of zinc sulphate, colour

Table 4.3: Turbidity and COD Removal Using Zinc Sulphate and Lime

ZnSO <sub>4</sub> mg/l	Lime mg/l	pH	Turb- idity NTU	Percent Turbidity Removal	COD mg/l	Percent COD Removal	Soluble COD mg/l	Percent Soluble COD Removal
00	00	5.12	155	-	5555	-	1919	-
20	100	5.00	140	9.6	5303	4.50	1919	-
20	200	5.00	135	12.9	5050	9.10	1919	-
20	300	5.20	100	35.5	5303	4.50	1818	5.30
20	400	6.00	45	70.9	4040	27.30	1717	10.50
20	500	6.30	40	74.2	4040	27.30	1616	15.70
20	600	7.50	37	76.1	4125	25.70	1666	13.20
20	700	8.50	32	79.3	3996	28.10	1630	15.10
20	800	8.70 (colour)	-	-	4340	21.87	1775	7.50
20	900	(colour)	-	-	-	-	-	-
30	100	5.00	140	9.6	5303	4.50	1919	-
30	200	5.20	80	48.4	5050	9.10	1919	-
30	300	5.20	80	48.4	5050	9.10	1919	-
30	400	6.14	40	74.2	4040	27.30	1616	15.70
30	500	6.40	34	78.1	4040	27.30	1565	18.45
30	600	7.47	37.5	75.8	4598	17.20	1738	9.40
30	700	8.12	32.5	79.0	3996	28.10	1557	18.86
30	800	8.80 (colour)	-	-	4520	18.60	1811	5.60
30	900	(colour)	-	-	-	-	-	-



Note.—Plotted data for metal sulfides based on experimental data listed in Seidell's solubilities.

SOURCE: Solubilities for metal hydroxides are taken from curves by Freedman and Shannon. "Modern Alkaline Cooling Water Treatment," in *Industrial Water Engineering* (p. 31), Jan.-Feb. 1973.

Fig. 4.8: Solubility of Zinc Hydroxide as a Function of pH. (EPA, 1980).

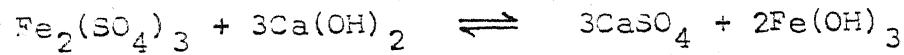
developed around pH 9. The colour of the samples were spectrophotometrically measured (after centrifugation to remove minute flocs) and found that it was around 360 colour units in platinum cobalt scale. This colour development may be due to zinc complex with colestrem present in the milk.

Figures 4.9 and 4.10 give an idea of turbidity, total COD and soluble COD removals for 20 mg/l and 30 mg/l  $ZnSO_4$  respectively. The turbidity removal and total COD removal seem to have some correlation upto a certain level. Some removal of dissolved COD is observed as the lime dosage increases. This removal may be due to adsorption of soluble organic molecules on to the gelatinous precipitate of zinc hydroxide.

Unlike the case of alum coagulation, the results with  $ZnSO_4$  show that the removal of suspended organic matter and soluble organic matter have no relation with each other. As can be seen in Figures 4.9 and 4.10, the suspended COD has not been removed to a large extent but soluble organics reduction is observed.

#### 4.4 Experiments with Ferric Sulphate:

The use of ferric salts as coagulants is common knowledge. However this practice was more prevalent before alum gained popularity. In certain experiments reported with these coagulants on domestic wastewater, removal of colloids have been good (Madhu Rani Sharma, 1983). The chemical reaction of ferric sulphate with lime are



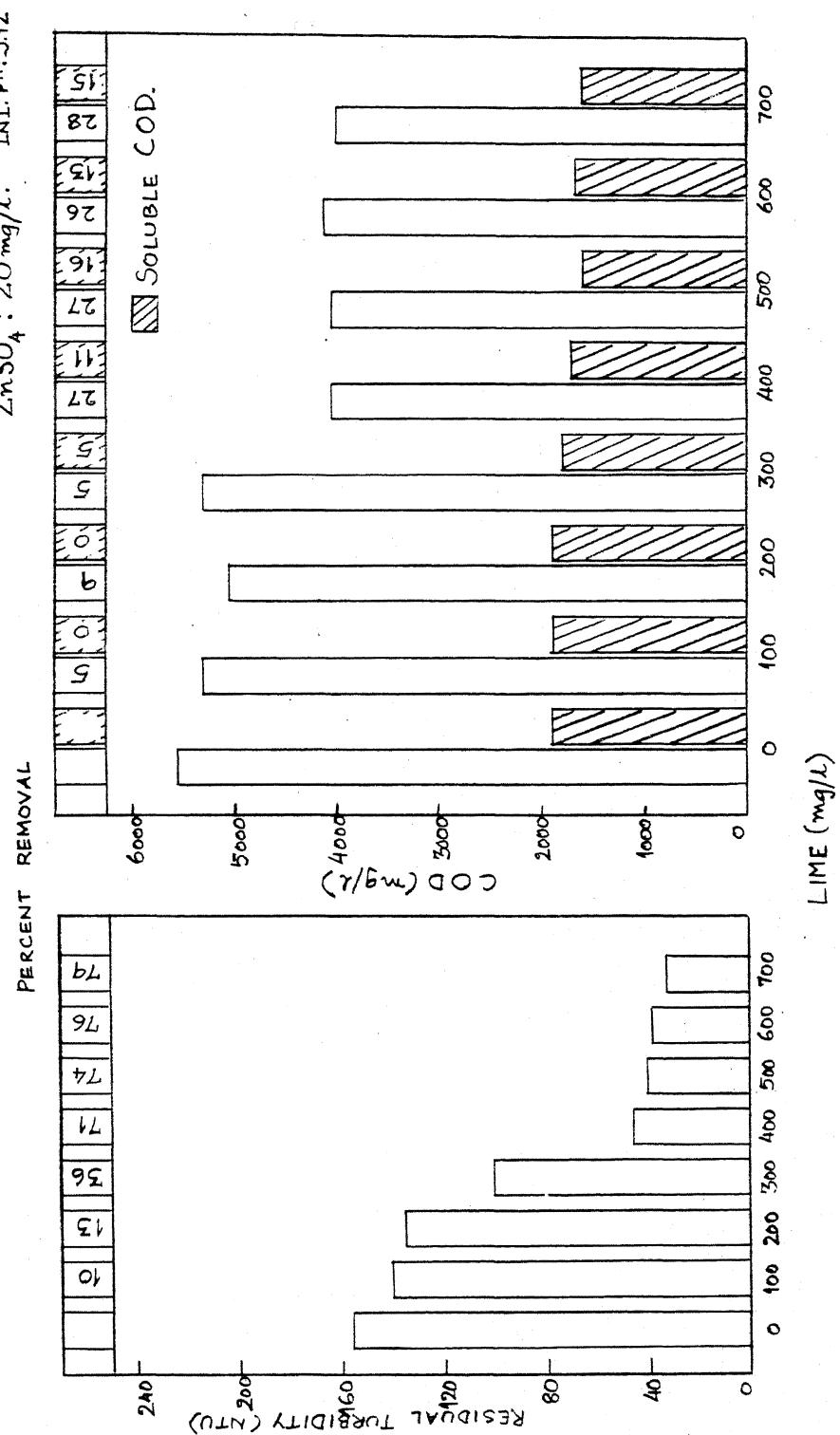


Fig. 4.9 : Turbidity, Total COD and Soluble COD Removal by Zinc sulphate and Lime : At 20 mg/l Zinc sulphate

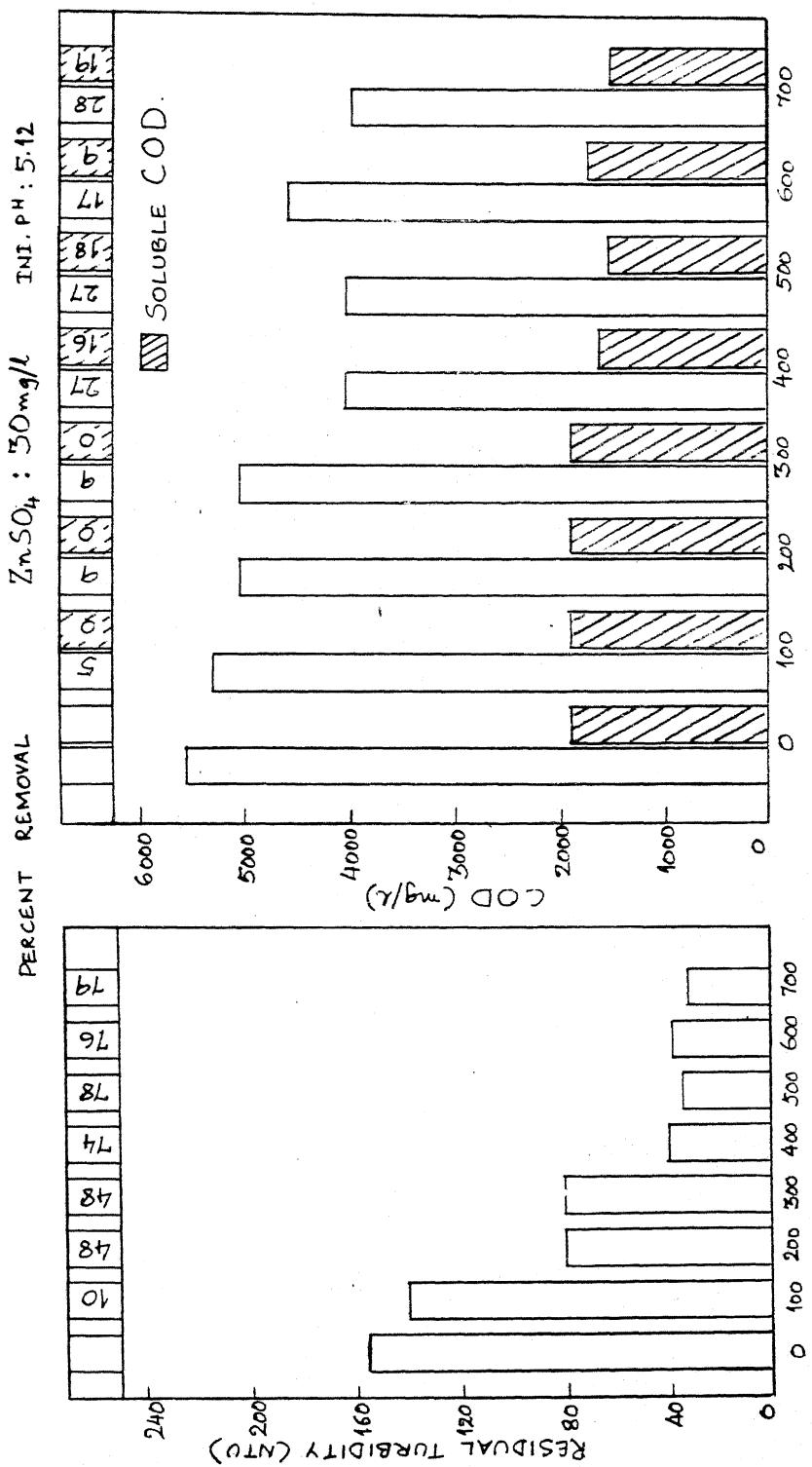


Fig. 4.10 : Turbidity, Total COD and Soluble COD removal by zinc sulphate and lime : At 30 mg/l Zinc sulphate.

Preliminary experiments with ferric sulphate were conducted with 25, 50 and 100 mg/l of the coagulant and 100-300 mg/l of lime. Lime doses were decided considering the minimum solubility of ferric hydroxide between pH 4 to 7 (Figure 4.11).

Removal of turbidity or COD was not appreciable as observed by the above experiments. In these cases, yellowish brown colour development was observed indicating that ferric hydroxide was still in the soluble form. By visual observation, 25 mg/l ferric sulphate dose seemed to give a better clarification.

Further experiments with higher dosages of lime to increase pH and alkalinity, at 25 mg/l ferric sulphate concentration, resulted in about 75 percent removal of turbidity but negligible reduction in COD (Table 4.4). No explanation could be given to this except for hypothesizing that some interference has crept in COD determination.

Hence further experiments were not conducted with this coagulant.

#### 4.5 Experiment with Ferric Chloride:

Next to alum, ferric chloride is the most popular among coagulants in water and wastewater treatment. Hence ferric chloride was used in coagulation and flocculation experiments. For different coagulant doses, varying from zero to 1000 mg/l at a pH of 6.15 which is in the range of optimum pH for ferric hydroxide formation, there was no removal of turbidity. Colour development was observed for all the doses. Hence investigation was not continued in this area.

#### 4.6 Adsorption Tests:

The failure of different coagulants to remove soluble organics from the dairy wastewater led to an interest towards

Table 4.4: Turbidity and COD Removal by Ferric Sulphate and Lime

Ferric Sulphate mg/l	Lime mg/l	pH	Turbidity NTU	Percent Turbidity Removal	COD mg/l	Percent COD Removal
0	0	5.94	77.5	-	4672	-
25	100	6.46	77.0	-	4420	5.3
25	200	7.11	22.5	71.0	4545	2.7
25	300	7.26	27.0	65.2	4444	4.9
25	400	7.80	27.5	64.5	4494	3.8
25	500	9.04 (colour)	-	61.3	-	-

Table 4.5: COD Removal by Adsorption on Sulphonated Coal and Animal Charcoal

Sorbent	Sulphonated Coal		Animal Charcoal		
	Dose mg/l	COD mg/l	Percent COD Removal	COD mg/l	Percent COD Removal
0	405	-	405	-	-
300	372	8.1	353	12.8	
500	402	-	363	10.4	
1000	392	3.2	373	7.9	
2000	392	3.2	363	10.4	
3000	402	-	363	10.4	
4000	402	-	373	7.9	

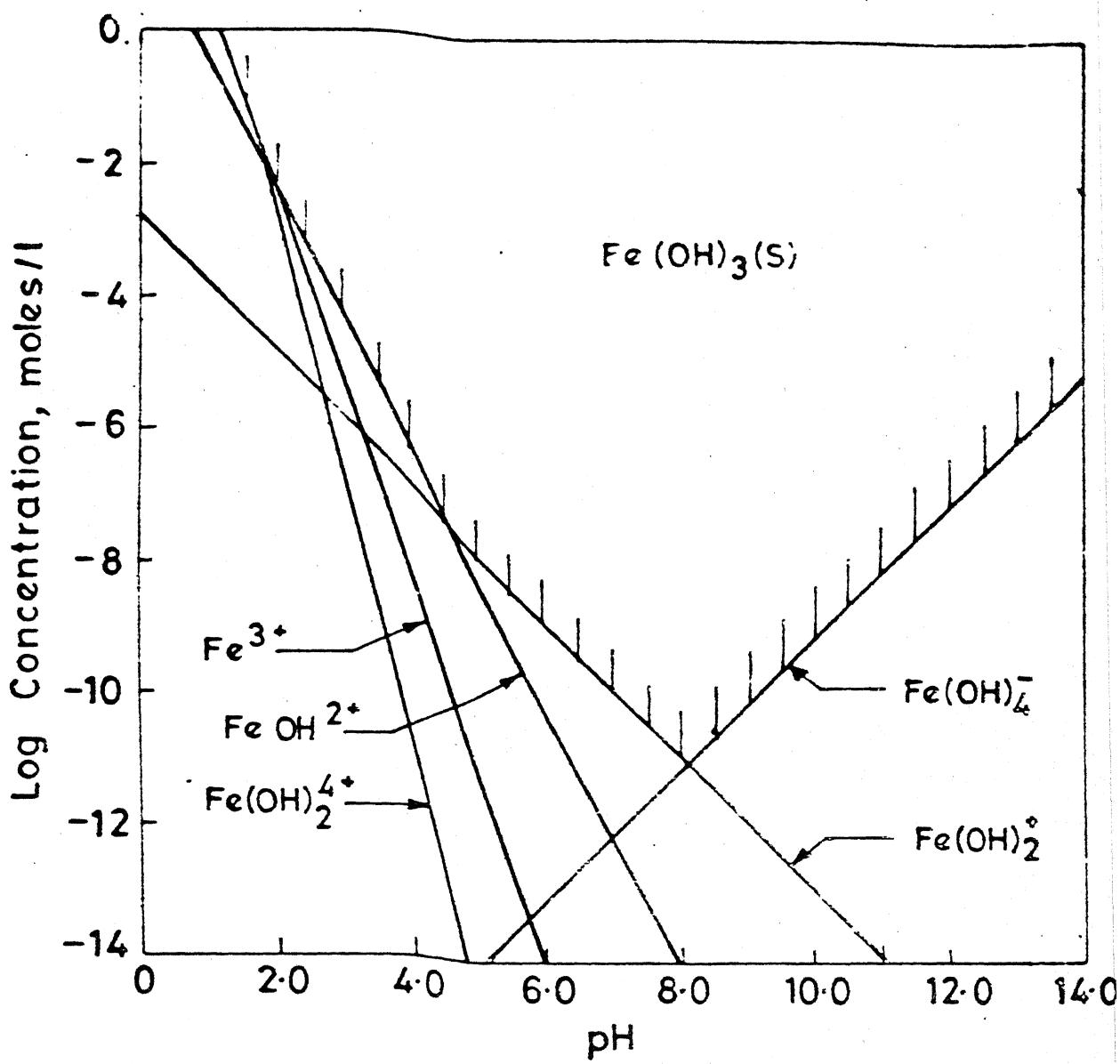


Fig. 4.11 Solubility Equilibria of Amorphous  $\text{Fe(OH)}_3(\text{s})$  at 25 °C (Weber, 1972)

adsorption process. Protein adsorption on activated carbon has been reported by Sugimoto et.al. (1976). Since activated carbon was not immediately available, tests were conducted with sulphonated coal and animal charcoal.

The adsorption tests were conducted on jar test supernatants. Results of these slop tests are given in Table 4.5. Tests conducted with sorbent dosages of 0-4 g/l gave negligible removal of soluble COD. Higher doses were not tried because the removal of COD did not increase with increase in sorbent doses.

#### 4.7 General Discussion:

The total study, unfortunately has not given encouraging results. It strengthens the notion that chemical treatment was not useful in reducing the soluble BOD. Some fifty percent of total COD could be removed initially with the use of alum by way of suspended solids removal. The wide variation in both quality and quantity of suspended solids and COD in the wastes over different time periods escaped the understanding in experimentation. Better planning could have yielded some better presentable results.

#### 4.8 Conclusions:

1. Coagulation and flocculation is useful in removing most of the suspended and a little of soluble organic matter represented by COD values.
2. Zinc sulphate removed more soluble organics than aluminum sulphate.

Q. 30 :-

3. Adsorbents like sulphonated coal and animal charcoal did not facilitate removal of soluble organics to any appreciable extent.
4. Chemical coagulation and flocculation can be used only to a limited extent for reducing COD and suspended solids in high BOD wastes like dairy waste.

## 5. SUGGESTIONS FOR FUTURE WORK

After conducting the investigations, the author finds that many a gap has emerged during the process of reporting the work, elucidation of which is needed but could not be pursued. Some of these are passed on for future work but are actually shortcomings of the present work.

1. Composite sampling may be used for experiments keeping in mind the sudden variation of waste strength and intermittent flow.
2. Further detailed study may be carried out on adsorption to investigate its removal of soluble organics in high strength wastewaters.
3. Other physicochemical methods may be tried for removal of soluble organics.
4. Other high strength organic wastes may be used for a similar study.

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## REFERENCES

- Ahmad, M.Z. (1985). 'Studies on Chemical Treatment of Wastewater'. M.Tech. Thesis, I.I.T., Kanpur.
- Agarwal, I.C. and Suriapandian, P.S. (1981). 'Removal of Dairy Waste Organics by R.B.C.s'. Indian Journal of Environmental Health, 23, 27.
- Alagarsamy, S.R. and Bhalerao, B.B. (1972). 'Treatment of Dairy Wastes by Mechanical Biological Methods'. Indian Journal of Environmental Health, 14, 225.
- Benefield, L.D., Judkins, Jr., J.F. and Weand, B.L. (1982). 'Process Chemistry for Water and Wastewater Treatment'. Prentice-Hall, Inc., New Jersey.
- Bull, M.A., Sterritt, R.M. and Lester, J.N. (1981). 'Methods Available for Treatment of Wastewater in the Dairy Industry'. Journal of Chem. Tech. and Bio. Tech., 31, 579.
- Cardoba, P.R., Sanchez, R.F. and Seneriz, F. (1984). 'Treatment of Dairy Industry Wastewater with an Aerobic Filter'. Biotechnology Letter, 6, 753; Poll. Abs., 85-00476 (1985).
- Doudoroff, P. and Katz, M. (1950). 'Critical Review of Literature on the Toxicity of Industrial Wastes and Toxic Components to Fish'. Sewage and Industrial Wastes, 22, 1432; quoted in Mohanrao, G.J. (1972). 'Dairy Waste Characteristics with Reference to ISI Standards'. Indian Journal of Environmental Health, 14, 218.
- E.P.A. (1980). 'Control and Treatment Technology for the Metal Finishing Industry - Sulfide Precipitation'. Technology Transfer, EPA 625/8-80-003.
- Himachal Pradesh State Cooperative Milk Producers' Federation Ltd., Shimla, H.P. (1986). Personal correspondence.
- Ling, E.R. (1956). 'A Text Book of Dairy Chemistry - Vol. 1'. Chapman and Hall Ltd., London.
- Madhu Rani Sharma (1983). 'Studies on Physico-chemical Treatment of Domestic Wastewater'. Ph.D. Thesis, I.I.T., Kanpur.
- Metcalf and Eddy, Inc. (1979). 'Wastewater Engineering'. McGraw Hill Book Company, New York.
- Mihaltz, P. and Czebo, L. (1984). 'Study of the Purification of Fat and Protein Containing Wastewaters by Means of Chemical Coagulation and Flotation'. Dev. Food Science (Eng.), 9, 347; Chem. Abs., 102:154250t (1985).

- Mohanrao, G.J. (1972). 'Dairy Waste Characteristics with Reference to ISI Standards'. Indian Journal of Environmental Health, 14, 218.
- Mohanrao, G.J. and Subramanyam, P.V.R. (1972). 'Sources, Flows and Characteristics of Dairy Wastes'. Indian Journal of Environmental Health, 14, 207.
- Nemerow, N.L. (1978). 'Industrial Water Pollution'. Addison Wesley Publishing Company, Massachusetts.
- Ronkainen, R. (1978). 'Planning and Use of Chemical Precipitation in Pond Water Purification'. Tutkimus Tek. (Finnish), 6, 62; Chem. Abs., 89:117152e (1978).
- Rao, M.N. and Datta, A.K. (1979). 'Wastewater Treatment'. Oxford and IBH Publishing Co., Calcutta.
- Satish Chand and Mehrotra, R. (1988). 'Evaluation of Aerobic Fluidised Bed Pilot Plant System for Dairy Waste Treatment'. Proc. of National Seminar on Management of Water and Wastewater Systems, Patna, Theme 6-9.
- Sawyer, C.N. and McCarty, P.L. (1978). 'Chemistry for Environmental Engineering'. McGraw Hill Book Co., New York.
- Saxena, K.L. and Subramanyam, P.V.R. (1978). 'Quantity and Characteristics of Wastewater from Dairies in India'. Bull. Intl. Dairy Fed. (Eng.), 104, 93; Chem. Abs., 89:220449f (1978).
- Singh, V., Palnitkar, S. and Agarwal, B.C.L. (1983). 'Treatment of Vanaspati Ghee Plant Effluent and Recovery of Oil'. Ind. Ass. of Water Pollution Control Tech. Annual, 10, 39; Poll. Abs., 85:03652 (1985).
- Standard Methods (1984). 'For the Examination of Water and Wastewater'. AWWA, APHA, WPCA, 15th edition.
- Sugimoto, M., Takagi, M. and Yoshii, H. (1976). 'Treatment of Wastewater from Food Plants with Activated Carbon V. Efficiency of GAC Using Several Wastewaters'. Aichi-Ken Shokuhin Kogyo Shikesho Nempo (Japan), 14, 102; Chem. Abs., 85:9916a (1976).
- Suneeth Kumar, S.M. (1987). 'An Investigation on Removal of Copper(II) by Sulphonated Coal from Aqueous Phase'. M.Tech. Thesis, I.I.T., Kanpur.
- Tabakov, D. (1979). 'Preliminary Treatment of Dairy Wastewaters by Electrolytic Coagulation Coupled with Other Methods'. Gaz, Woda Tech. Sanit. (Pol.), 53, 356; Chem. Abs., 93: 119683k (1980).

Tabakov, D. (1984). 'Treatment and Utilization of Wastewater from Dairy Industry'. Molochn. Prom-St., 11, 43; Chem. Abs., 102:66826e (1985).

Tabakov, D. (1984a). 'Investigation of Electric Flotocoagulation and Improvement by Treating Effluent Waters from Dairy Industry and Possibilities of Utilizing the Recovered Protein Complex'. Dev. Food Science (Eng.), 9, 253; Chem. Abs., 102:154248y (1985).

Taori, K.B., Dhabadgaonkar, S.M. and Raman, V. (1983). 'Dairy Waste Treatment by Anaerobic Packed Bed Upflow Filter'. Ind. Ass. of Water Pollution Control Tech. Annual, 10, 21; Poll. Abs., 85:3655 (1985).

Verma, S.R., Dalela, R.C., Tyagi, M.P. and Gupta, S.P. (1974). 'Studies on the Characteristics and Disposal Problems of the Industrial Effluents with Reference to ISI Standards: Part-I'. Indian Journal of Environmental Health, 16, 289.

Weber, Jr., W.J. (1972). 'Physicochemical Processes for Water Quality Control'. Wiley-Interscience, New York.